Time-Resolved EPR Studies on Photochemistry of Compounds Containing Group 14 Elements and Others

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論 文 内 容 要 旨

Chemical reactions, specially the reactions initiated by photon are very important in chemistry. The control and application of reactions are largely depend on the photochemical and photophysical properties of short-lived transient reaction intermediates such as radicals and excited triplet molecules and their interactions. In this thesis, we discussed the photochemical and photophysical properties of the reaction intermediates and their interactions in order to understand a photochemical reaction. Time resolved electron paramagnetic r esonance (TREPR) is one of the most powerful methods, which provides direct information about structures and dynamics of the short lived paramagnetic species.

In this work all EPR measurements were carried out on a X- band JEOL-JES-FE 2XG EPR spectrometer with a modified fast amplifier. Samples were excited inside the EPR cavity by a Nd:YAG (Spectra Physics GCR-170) or an OPO (Spectra Physics, MOPO-710) laser. Compounds containing the group 14 element need a shorter wavelength for excitation such as 266 nm. An ordinary dewar gives strong artificial TREPR signals with the short wavelength excitation. Under such circumstances a special three cylinder dewar was designed to carry out variable low temperature EPR measurements. The measurements other than the 266 nm excitation were done by using a JEOL ES -DVT3 liquid N_2 gas flow system.

1. The Lowest Excited Triplet States of α -Silyl and α -Germyl Ketones

The triplet properties of a series of a-M ketones (M = Si, Ge) have been investigated in relation to their interesting characteristic spectral properties, which are markedly different from their carbon analogous. The following M-ketones were investigated.

I. $PhMe_2SiCOPh$ II. $Me_3SiCOPh$ III. $Ph_3GeCOPh$ IV. $PhMe_2GeCOPh$ V. $Me_3GeCOPh$

The ZFS parameters of the triplet states including spin-orbit couplings have been studied extensively for C-ketones, where $^3n\pi^*$ and $^3\pi\pi^*$ states are very close and heavily mixed and T_1 is $^3\pi\pi^*$ in many cases. The $^3n\pi^*$ state ketones can be shifted with a change of substituents or/and environment and T_1 becomes $^3n\pi^*$ or $^3\pi\pi^*$, with mixing of each other. But compounds containing almost pure T_1 ($n\pi^*$) or T_1 with a little $\pi\pi^*$ mixture are not normally available and very few cases have been studied so far. M-ketones (M =Si, Ge) possess almost pure T_1 ($n\pi^*$) state, as T_1 ($n\pi^*$) and T_2 ($\pi\pi^*$) states are separated by an energy of more than 4000 cm^{-1}.

In this part, our aims are (i) to analyze the ZFS parameters of the lowest excited triplet states of nearly pure T_1 ($n\pi^*$) molecules (M-ketones) in terms of spin-orbit coupling induced $^3n\pi^*$-$^{1,3}\pi\pi^*$ mixings, (ii) to measure the extent of electron delocalization on a metal, which is responsible for the large red shift in the absorption spectra and its substitutent effect using EPR parameters, and finally (iii) to analyze a little $\pi\pi^*$ character in the T_1 ($n\pi^*$) state of the α -M ketones.

Triplet properties such as ZFS, g, and populating rates, of a series of M-ketones were obtained by simulating observed EPR spectra. The obtained TREPR spectra of these molecules show that the sublevel scheme and populating rates are similar. In these molecules spin-orbit interactions due to carbonyl oxygen and metal play important roles for the spin selective intersystem crossing from singlet to triplet states, and T_z sublevel is dominantly populated, where the z axis is parallel to the carbonyl group (C=O). Triplet sublevels were assigned by the magneto-photoselection (MPS) experiment under selective excitations to S_1 ($n\pi^*$) and S_2 ($\pi\pi^*$) states by 450 nm and 266 nm

UV lights, where the directions of the S_0--> S_1 and S_0–> S_2 transition moments are along x and y axes of these molecules, respectively. From the MPS spectra, triplet sublevels are identified as T_y, T_x, and T_z from the top to the bottom.

The obtained *D* values of these molecules show that the T_1 state are nearly pure $n\pi^*$ in character and the *D* value decreases from molecule I to V. There are two main contributions to ZFS parameter D: (i) spin dipole (D_{ss}) and (ii) spin-orbit (D_{so}) interactions and *D* consists of a sum of these two contributions. The change of *D* is attributed to the change of D_{so} and explained by a proposed spin-orbit induced $^3n\pi^*$ (T_1) and $^{1,3}\pi\pi^*$ (S_2, T_2) mixings scheme. According to this scheme D_{so} is negative and the magnitude increases from molecule I to V. The magnitude of Dso increases from Si to Ge containing molecules due to the larger spin-orbit coupling constant of germanium than silicon.

The characteristic spectral properties such as the remarkable red shift in the absorption spectrum, of these molecules largely depend on the delocalization of the n and π orbitals of oxygen over the metal. The electron density (mixing coefficient) on the metals were obtained from D_{so}, which increases with methyl substitution on metal. Among the same metal containing molecules the magnitude of D_{so} increases with the mixing coefficient on metal and the order is similar to that of the T_1 energy. It is also found from D_{so} that a weak $\pi\pi^*$ character in the $T_1(n\pi^*)$ state increases from molecule I to V.

The g values are obtained from spectral simulation and are the same as that of the free electron value. The calculated g value (using D_{so}) is consistent with the experimental value, which supports our proposed spin-orbit coupling scheme.

Solvent polarity produces a substantial effect on the D value, where D_{so} increases with solvent polarity. This indicates an increase of a $\pi\pi^*$ character in the $T_1(n\pi^*)$ state and is consistent with the obtained T_1 lifetime.

The triplet properties of α-M ketones show that these are nearly pure T_1 ($n\pi^*$) molecules and a little $\pi\pi^*$ character increases with methyl substitution and solvent environment.

2. Photolysis of Compounds Containing Group 14 Elements

Chemically induced dynamic electron polarization (CIDEP) has been widely studied by TREPR spectroscopy that gives valuable information concerning intermediate radicals and precursor excited states of the reaction. Comparatively few studies have been made of CIDEP phenomena in systems involving inorganic materials. Those widely used are organic ketones and quinones.

Photolysis of hexaphenyl disilane, digermane, and distannane would give rise a triphenyl silyl, germylene, and stannyl radical, respectively. There is no EPR study of these radicals in fluid solution. Our aim is to extent the CIDEP study including group 14 element centered (Si, Ge, Sn) radicals through observations of CIDEP signals in solution and to explain the mechanism of the photochemical reaction with proper identification of intermediate radicals and analysis of their dynamics.

CIDEP signal of $Ph_3Si.$ and $Ph_3Ge.$ radicals were observed in solution for the first time under direct photolysis of $Ph_3Si\text{-}SiPh_3$ and $Ph_3Ge\text{-}GePh_3$ using high energy (266 nm) UV-irradiation. In both cases the obtained emissive CIDEP signals were explained by the triplet mechanism (TM), indicating that these reactions occur from the excited triplet states. Spin-lattice relaxation times were obtained from decay analyses. The CIDEP signals were also observed on the ^{29}Si isotope in the $Ph_3Si.$ radical. The signal was explained by the mixed ST_0 and TM mechanisms. We also obtained electron density (13.4%) on the 3s orbital of the silicon atom from the isotropic hyperfine coupling constant.

3. Electron Spin Polarization Transfer from Photo-Excited Triplets to a Radical

Recently two CIDEP mechanisms have been proposed for radical-triplet systems as the radical-triplet pair mechanisms (RTPM) and the electron spin polarization transfer (ESPT). The spin polarization due to RTPM has been reported rather extensively and is known to be generated from electron spin dipolar, Zeeman, and hyperfine couplings between quartet and doublet states, which are formed by an electron spin exchange interaction ($H_{ex} = -2JS_R \cdot S_T$) between R and T. On the other hand, for the ESPT a triplet polarization generated from a sublevel selective intersystem crossing is transferred to a radical through an exchange interaction. Although some observations had been likely to be interpreted by the ESPT, no conclusive results were reported so far. The first definitive assignment of the ESPT has been given for a triplet porphyrin-nitroxide radical system. In this part, we have demonstrated another evidence of ESPT to show that it does not only occur in porphyrin-nitroxide radical systems, as unique properties of these systems, but it is also possible to occur in other systems with the proper choice of triplets and radicals. We have studied spin polarization transfer from photo-excited triplet metallophthalocyanine (MTNPc) to a radical (TEMPO), on the basis of analyses of TREPR spectra and decay curves of both MTNPc and TEMPO signals in solution.

TREPR spectra of the excited triplet (T_1) states of H_2TNPc and ZnTNPc in solution were observed as an emission and an absorption of microwave, respectively. The decay time profile of the T_1 H_2TNPc signal shows two different polarizations as E (emission) at early and A (absorption) at later times, whereas in the case of T_1 ZnTNPc both the polarizations are absorptive. The decay of the T_1 MTNPc signals were analyzed by a double exponential function, and the fast (early) and the slow (later) decay components are assigned as the spin-lattice relaxation (SLR) and the intrinsic triplet lifetime, respectively. It is found that the SLR time decreases with temperature and is faster for T_1 ZnTNPc than for T_1 H_2TNPc.

CIDEP signals of the polarized TEMPO were observed in MTNPc-TEMPO (M = Zn, H_2) systems. In both cases two kinds of polarizations were observed at early and later times. The early time polarizations are emissive and absorptive for H_2TNPc- and ZnTNPc-TEMPO systems, respectively and are same as those of the corresponding triplet polarizations. Whereas, the late time polarizations were all emissive irrespective of MTNPc. The decay of the early time polarization is the same as that of the spin-lattice relaxation time of TEMPO and the late time polarization decays with the corresponding triplet lifetimes. The early and the late time polarizations on TEMPO were interpreted in terms of the electron spin polarization transfer (ESPT) from T_1 to the radical and the radical-triplet pair mechanism (RTPM) with a quartet precursor under $J < 0$ (J; exchange coupling parameter), respectively.

The ESPT rate (k_{ESPT}) was determined from the decay analysis of the T_1 signals and found that k_{ESPT} decreases with lowering temperature and is faster in the ZnTNPc system. It is also found that the ESPT rate is much slower than the diffusion rate in the H_2TNPc system and axial ligation of TEMPO remarkably accelerates the ESPT rate in the ZnTNPc system.

In these systems we also obtained the triplet quenching rate (k_q) which includes the RTPM process. The quenching process is much slower at least by two orders of magnitudes than the ESPT process. This might be due to the higher excited doublet (D_1) state (ca.18000 cm^{-1}) of TEMPO than T_1 MTNPc (14000-16000 cm^{-1}), where no energy transfer occurs from T_1 to D_1.

論文審査の結果の要旨

イスラムサイフル提出の論文は，これまでほとんど検出されたことのないケイ素，ゲルマニウムなどの１４族元素を含む化合物の光化学反応における反応中間体を，電子スピン共鳴(ESR)で観測した研究である。ESR 法は，過渡吸収法に比べて反応中間体の電子構造や分子構造に関して質の高い情報を与えるが，時間分解能や感度に関して著しく劣っていた。しかし，時間分解ESR法では，時間分解能も80ナノ秒程度まで向上し，三重項からの反応であれば，ほとんど問題のないところまできている。本研究では，励起三重項状態の電子構造の決定，反応中間体の捕捉と電子状態の解析，電子スピン分極移動機構の解明を目的として，３つの系について時間分解ESR法を用いた研究を行った。得られた結果は，次のようにまとめられる。

１）α位にケイ素およびゲルマニウム元素をもつカルボニル(>C=O)を合成して，励起状態の性質を調べた結果，最長波長部の吸収は$^{1}n\pi^{*}$で，C-カルボニルに比べて，著しくレッドシフトしていることがわかった。これらの化合物の励起三重項のESR スペクトルを観測・解析して，三重項状態がほぼ純粋な$^{3}n\pi^{*}$であることを見い出した。

２）置換基および溶媒効果から，これらの化合物の励起三重項ESR パラメータ，項間交差速度と三重項寿命を$^{3}n\pi^{*}$にわずかに混じる$^{1,3}\pi\pi^{*}$性で解析することができた。$^{3}n\pi^{*}$と$^{3}\pi\pi^{*}$の混合については，カルボニルで非常に多くの研究例があるが，ほぼ純粋な$^{3}n\pi^{*}$系の研究は初めてである。

３）ヘキサフェニルジシラン，ジゲルマンの光化学反応の中間体トリフェニルシラン，ゲルマンを初めて溶液中のESRで観測した。スペクトルには，核スピンを持つ^{29}Siの超微細相互作用が観測され，その大きさからケイ素上のスピン密度が0.13と求められた。

４）フタロシアニン励起三重項とラジカル間のスピン分極移動の研究を行い，励起三重項とラジカルのスピン分極が一致すること，前者の信号の減衰と後者の信号の立ち上がりが一致することから，スピン分極移動を定量的に実証した。

これらの成果は，本人が自立して研究を行うに必要な能力と学識を持つことを示している。よって，イスラムサイフル提出の論文は，理学博士の学位論文として合格と認める。